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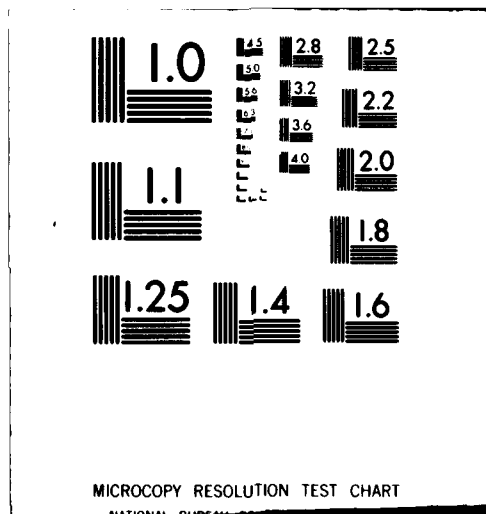
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STATISTICAL MECHANICAL STUDY OF POLYVINYLIDENE FLUORIDE

FINAL REPORT

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P. L. TAYLOR AND A. J. HOPFINGER

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A theoretical study of polyvinylidene fluoride has been performed in which calculations have been made of the equation of state, of the piezoelectric and pyroelectric coefficients, and of the mechanism of poling of β -phase material. Transfer-integral and mean-field methods have been used →		

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to derive the free energies of the various phases, and thence to derive the thermodynamic variables as functions of temperature, stress, and applied electric field. The poling process whereby electrical activity is induced in β -phase material has been studied in a model in which solitary waves of rotation are induced by temperature and applied electric fields and propagate along a chain axis. The rate of spontaneous creation of these kinks of polarization and their velocity have been used to predict the times necessary for poling material under various conditions.

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FINAL REPORT

The performed research consisted of a theoretical study of both equilibrium and non-equilibrium properties of poly(vinylidene fluoride), hereafter referred to as PVF_2 . This material can exhibit strong piezoelectric and pyroelectric effects if suitably prepared, and is consequently of great technological interest. The study consisted of a series of calculations of the equation of state, and the mechanism by which electrical activity is induced.

Detailed accounts of the results of our investigations have been given in Refs. 1-9, and so we here just provide a brief summary of some of the more important aspects of our work.

(i) Equation of state and crystal structures

The free energy of an assembly of interacting chains of PVF_2 was calculated in a formalism whose starting point was close to first principles. The potential energies of interaction of various pairs of atoms were calculated by using molecular orbital techniques and molecular mechanics, and these potentials were then used in a study of the statistical mechanics of an assembly of interacting chains. The basic technique involved the precise solution of a model of a single chain in a potential field that was expressed as a mean-field approximation to the true interchain potential. The resulting set of equations was solved self-consistently to yield the Helmholtz and Gibbs energies.

A rich variety of phases emerged from this calculation, and it was gratifying that the phase predicted to be most stable was indeed the phase-II, or α -phase, crystal structure. Of the other phases found in this work the β phase was predicted to have a higher free energy than the α phase, and thus to be only metastable; application of a uniaxial stress, however, was

found to lower the free energy of the β phase sufficiently to make it the most stable, in accord with experiment. These results are central to our studies of PVF_2 , and are described in detail in Refs. 1 and 2.

Other work related to the stability and existence of various crystal structures includes some studies^{3,4} of possible conformations for the phase-III form of PVF_2 , and a general review of the application of our transfer-integral techniques to polymer properties⁵. Some of the support for this aspect of our research was received from the N.S.F. Materials Research Laboratories at Case, in addition to the principal support from the A.R.O.

(ii) Piezo- and pyroelectric coefficients

The large observed piezoelectric effects in PVF_2 have been conjectured to arise from a variety of causes¹⁰. Of these we have studied in particular the contributions from changes in shape of a sample under stress (that is, the second piezoelectricity) and from effects at the boundary between amorphous and β -phase material. While secondary effects can explain much of the observed coefficient, there appears to remain a further component requiring an alternative explanation, and to this end we have looked at a model in which stress-induced reversible crystallization can enlarge the size of a β -phase crystallite at the expense of amorphous material⁶.

In the course of this study it was discovered that the thermodynamics of piezoelectric devices involving polymers does not appear to be completely understood. Contributions to the free energy arising from size changes of an electrode plated to a polymer film can produce forces that are absent from most treatments of piezoelectric devices. While these forces may produce negligible effects in ceramic ferroelectrics they can apparently be significant in a comparatively soft polymer, and need careful treatment⁷.

(iii) Poling of PVF₂

The production of piezoelectric material by annealing β -phase film in a large electric field has been studied in a model in which a reorientation occurs of the zigzag planar chain about its axis. The equations of motion for this process are highly nonlinear, and lead to consideration of a propagating solitary wave of polarization. These "kink" solutions have been studied in a model in which the chain rotates by 180° about its axis⁸ and also in one in which a 60° rotation occurs, accompanied by a small change in lattice dimensions⁹, as had been suggested by Kepler and Anderson. The model involving rotation by 60° gives the better agreement with experimentally observed poling times.

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